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COMPLETE SPECIFICATION

Preparation of Mixed Glycerol Ester Compositions

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, 5 New York, United States of America (assignee of NORRIS DEAN EMBREE and GEORGE YOUNG BROKAW), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method 10 by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing mixed glyceride materials, and 15 more particularly to a cyclic process for preparing compositions containing a substantial amount of a mixed glycerol ester having at least one lower acyl radical, and at least one higher acyl radical.

20 The present mixed glycerol esters are "tailor-made" fatty materials which have many useful properties not found in naturally occurring fatty materials. Mixed glycerol esters have many applications, both 25 for food and non-food uses. Specifically, mixed glycerol esters can be used as coatings for such food as hams, weiners, raisins and nuts to reduce dehydration and rancidity; and as plasticizers in such foods as 30 margarine-like spreads and shortenings, in such cosmetics as hand creams and hair dressings, and in plastics such as polyvinyls, polyvinilidenes, and cellulose esters. Likewise mixed glycerol esters have utility as 35 lubricants and release agents. Other uses include coatings for medicinal-containing pills and tablets, components in suppositories, components in emulsions for intravenous injections, and special dietary fats. 40 It is accordingly desirable to have a simple process adaptable to the commercial preparation of such "tailor-made" materials.

An object of this invention is to provide a cyclic process suitable for preparing 45 "tailor-made" fatty compositions containing

substantial amount of mixed fatty glycerol esters.

According to the present invention, which is an improvement in or modification of the process claimed in Claim 1 of British Patent 50 No. 745,566, mixed glycerol ester compositions are prepared by reacting a higher acylated triglyceride and a hydroxyl radical-containing reactant comprised of, (1) glycerine with a lower acylated triglyceride, or, 55 (2) a lower acylated glycerol partial ester comprising glycerine and a mixture of lower acylated glycerine, in the presence of a basic transesterification catalyst, and the resulting reaction mixture is thereafter subjected to 60 vacuum distillation effective to separate therefrom remaining portions of the hydroxyl radical-containing reactant, the residue resulting from the first distillation is subjected to thin film vacuum distillation 65 effective to separate therefrom a composition containing a substantial amount of a mixed glycerol ester having at least one lower acyl radical and at least one higher 70 acyl radical, the resulting second distillation residue and the separated remaining portions of the hydroxyl radical-containing reactant are combined with additional portions of make-up composition comprised of 75 higher acylated triglyceride and the hydroxyl radical-containing reactant, and the above sequential steps repeated.

The term "mixed glycerol ester" used herein refers to glycerides containing at least one lower acyl radical and at least one 80 higher acyl radical.

The lower acyl radical comprising the lower acylated materials employed in the present process is any acyl radical having from two to six carbon atoms. Lower 85 acylated materials having acetyl or butyryl radicals are preferred.

Any higher acylated triglyceride containing acyl radicals having at least eight carbon atoms, suitably from eight to twenty-four 90

carbon atoms, and desirably from twelve to twenty carbon atoms, can be employed, the straight chain fatty acid radicals being more generally utilized. Higher fatty triglycerides containing fat-forming fatty acids, such as the triglycerides of animal fats and vegetable oils, are preferably employed. The higher acylated triglycerides can be either hydrogenated or unhydrogenated, the degree of hydrogenation being a variant in determining the physical properties of the mixed glycerol ester product. Examples of suitable higher acylated triglycerides include, trilaurin, tripalmitin, triolein, trilinolein and tristearin, and such naturally occurring triglycerides as are found in lard, beef tallow, cottonseed oil, soybean oil, peanut oil, coconut oil, and in other related fatty materials. The term "fat-forming fatty acid radical" used herein refers to higher acyl radicals derived from naturally occurring fats and oil, whether hydrogenated or unhydrogenated.

The make-up materials for the present reaction can be comprised of a higher acylated triglyceride, glycerine, and a lower acylated triglyceride containing acyl radicals having from two to six carbon atoms. Suitable lower acylated triglycerides include triacetin, tripropionin, tributyrin, triisobutylin, trivalerin and tricaproin, with triacetin and tributyrin being preferably employed. Such make-up materials can be fed into the reactor as a mixture, or as separate streams of higher acylated triglyceride, lower acylated triglyceride and glycerine. However, lower acylated triglycerides such as triacetin are relatively insoluble in glycerine. To facilitate the reaction, and to simplify feeding the reactor for continuous operation, a substantially single phase premixture composition comprised of lower acylated glycerol partial ester is preferably employed in lieu of glycerine and lower acylated triglyceride as make-up materials. Such a premixture composition can be prepared for example, by reacting glycerine and a lower acylated triglyceride in the presence of an interesterification catalyst, or, by reacting glycerine and a lower acyl anhydride. A typical premixture composition contains the partial esters monoacetin and diacetin, plus portions of triacetin and glycerine. A further typical premixture composition contains the partial esters monobutylin and dibutylin plus portions of tributyrin and glycerine. Either of these premixtures is combined with a higher acylated triglyceride to comprise one form of the make-up materials employed in the present reaction.

In accordance with this invention, the reactants are subjected to a transesterification reaction in the presence of a basis transesterification catalyst. The term "transesterifica-

tion reaction" is a generic term which includes the alcoholysis and ester-ester interchange types of reaction. Any of the well-known basic transesterification catalysts can be used including alkali and alkaline earth metals, hydrides, glyceroxides, hydroxides, and soaps, the bivalent alkaline earth metal hydroxides being preferably employed. Suitable basic transesterification catalysts include sodium metal, sodium hydride, sodium and potassium glyceroxides, sodium hydroxide, calcium hydroxide, strontium hydroxide, sodium stearate and similar well-known basis transesterification catalysts. The amount of catalyst can be varied in accordance with usual transesterification practice, with amounts of from about 0.001% to about 1% and particularly from about 0.005% to about 0.1% by weight based on the total weight of the reaction mixture being preferably employed. The basic transesterification catalyst is not substantially destroyed during the reaction and the successive distillations and recycles.

The reaction is preferably effected at elevated temperatures of at least 180°C. and more generally higher than about 200°C., with temperatures in the range of 230°C. to 260°C. being eminently suitable. The reaction time is usually from about 15 minutes to about 6 hours depending on the ratio of the reactants, concentration of catalyst, reaction temperature and similar variables affecting the speed of the reaction. The present cyclic reaction can be arranged so that fresh make-up materials and recycle materials are continuously fed into one portion of the reaction zone while reacted materials are continuously withdrawn from another portion of the reaction zone. In such an arrangement the reaction period is merely the average time that given portions of the reactants remain in the reaction zone.

Numerous reaction products result from the present reaction. However, these reaction products can be divided into distinct distillation groups which can be substantially separated by the present process. For example, a reaction between a higher acylated triglyceride such as tristearin, glycerine and lower acylated glycerine such as triacetin results in numerous reaction products which can be divided into four main Groups, these Groups being substantially separable by vacuum distillation, and more particularly by thin film vacuum distillation. Reaction products include:

GROUP 1	
Glycerine	
Monoacetin	125
Diacetin	
Triacetin	
GROUP 2	
Monostearin	
Monoaceto monostearin	130

Diaceto monostearin

GROUP 3

Distearin

Monoaecio distearin

5 GROUP 4

Tristearin.

The actual number of compounds in the respective Groups is, of course, multiplied by the existence of space isomers of the various compounds. The acetyl and stearyl radicals in the above Groups are merely illustrative of other lower and higher acyl radicals described herein.

The components in Group 1 comprise the distillate resulting from the first distillation of the present process. Any suitable vacuum distillation means can be employed that will remove substantially all of the components in Group 1 from the other components of the reaction mixture without decomposition or discoloration of the reaction products, thin film vacuum distillation being particularly effective. As the lower acylated glycerines of Group 1 in general are extremely bitter materials, particularly such materials as triacetin and tributyrin, it is ordinarily the practice to remove these components when the separated mixed glycerol ester composition is used in food products. Suitable distillation apparatus includes thin film high vacuum molecular stills of the centrifugal type, or of the falling film type, or other related thin film vacuum distillation apparatus operated in accordance with well-known vacuum distillation practice.

The distillation residue resulting from the first distillation is comprised substantially of Group 2, Group 3 and Group 4 components. This distillation residue is subjected to thin film vacuum distillation under conditions effective to distil therefrom substantially all of the components in Group 2, the components of Group 3 and Group 4 comprising the distillation residue of this second distillation.

The distillate resulting from the second distillation (the components of Group 2), is a composition comprised of substantial amounts of mixed glycerol esters having a higher acyl radical, a lower acyl radical and a hydroxyl radical. Such compositions are commonly called "lower acylated monoglycerides." A typical Group 2 composition can be obtained by reacting a 50% acylated glycerine premixture with fully hydrogenated lard at a ratio of about 4 parts of premixture to about one part of lard for about 1- $\frac{1}{2}$ hours at 250°C. in the presence of a basic transesterification catalyst such as 0.08% calcium hydroxide. The components of "Group 1" can be removed from the resulting reaction mixture by thin film vacuum distillation at temperatures up to about 135°C. and at a pressure of about 15 microns of mercury. The "acetylated

monoglyceride" can be separated from the resulting first distillation residue by thin film vacuum distillation at temperatures up to about 185°C. and at a pressure of about 15 microns of mercury. These conditions may be varied somewhat in accordance with well-known vacuum distillation practice. A major component in the resulting distilled product is a mixed glycerol ester having an acetyl radical, at fat-forming fatty acid radical, and a hydroxyl radical. The prepared "acetylated monoglyceride" is a soft, waxy solid at room temperature having a melting point of about 42°C.-44°C. Further, this product is non-greasy, has good flexibility in thin films, and is extremely resistant to oxidative rancidity.

The distillation residue resulting from the second distillation (the components of Group 3 and Group 4), and the distillate resulting from the first distillation (the components of Group 1), are recycled and combined with additional amounts of higher acylated triglyceride and hydroxyl radical-containing reactant make-up materials, and the above described sequential steps repeated, to effect a cyclic process. In a continuous process, recycle materials and make-up materials are continuously fed into the reaction zone. Likewise, the successive distillations are effected continuously in a continuous process. In the present process it is desirable to add additional and predetermined amounts of make-up materials in amounts substantially equivalent to the amount of product removed. That is, the make-up materials and the mixed glycerol ester-containing product are comprised of substantially equal amounts of materials and substantially equal proportions of higher acyl radicals, lower acyl radicals and hydroxyl radicals. The catalyst is not inactivated prior to the successive distillations, accordingly, the distillations are made from active catalyst. The catalyst is re-cycled and utilized again.

The present process can also be used to separate the Group 3 components from the original reaction mixture, Group 3 components being comprised of substantial amounts of a mixed glycerol ester having a lower acyl radical and two higher acyl radicals. This can be readily accomplished by subjecting the distillation residue resulting from the second distillation to further thin film vacuum distillation effective to separate the Group 3 components from the Group 4 component. Typical distillation conditions effective to distil Group 3 components from a composition resulting from the above-described reaction between a 50% acetylated glycerine premixture and fully hydrogenated lard after the components of Group 1 and Group 2 have been separated therefrom are at temperatures up to about 220°C.

and at a pressure of about 15 microns of mercury. As before, these conditions may be varied somewhat in accordance with known distillation practices. The residue 5 from the resulting distillation is thereafter re-cycled with the distillate resulting from the first distillation (the components of Group 1).

The above described sequence of steps can 10 be modified to prepare preferentially the components of Group 3. For example, the reaction mixture can be subjected to thin film vacuum distillation conditions effective to co-distil the components of Group 1 and 15 Group 2, the desired components of Group 3 thereafter being distilled from the resulting residue as described above. Also, the present process can be modified to prepare compositions comprised of both Group 2 20 and Group 3 by selecting suitable distillation conditions in accordance with known distillation practice.

The "tailor-made" fatty materials prepared by the present process, like naturally 25 occurring fatty materials, are mixtures of various components. The present "tailor-made" fatty materials are comprised substantially of the components of Group 2 and/or Group 3. The properties of such 30 prepared fatty materials can be varied by varying the nature of the lower and higher acyl groups. For example, an "acetylated monoglyceride" derived from lard may be a liquid, while an "acetylated monoglyceride" 35 derived from fully hydrogenated lard may be a solid. Similarly, certain butyrate fats may be liquid while the corresponding acetylated fat may be solid. Accordingly, 40 compositions having a wide range of physical properties can be prepared by the present process.

Likewise, the proportions of the various components within Group 2 and Group 3 can be varied to further widen the range of 45 physical properties obtainable by the present process. This can be accomplished to a large extent by varying the molar ratio of lower acyl radicals to hydroxyl radicals in

50 the reaction mixture (e.g. $\frac{\text{acetyl}}{\text{hydroxyl}}$ ratio).

In the preparation of acetylated materials, for example, this can be accomplished by 55 varying the degree of acetylation of the glycerine in the premixture composition, or, by varying the triacetin to glycerine ratio in the reaction mixture. In the preparation of Group 2 and Group 3 compositions, molar ratios of lower acyl radicals 60 to hydroxyl radicals are more generally varied from about 1/10 to about 10/1 in the reaction mixture. Within Group 2, to prepare compositions containing maximum amounts of mixed glycerol esters containing 65 a higher acyl radical, a lower acyl radical

and a hydroxyl radical, molar ratios of lower acyl radicals to hydroxyl radicals in the reaction mixture ranging from about 1/5 to about 5/1 are preferably employed. Mixed glycerol esters containing a higher 70 acyl radical and two lower acyl radicals can be prepared in proportionately high amounts within Group 2 compositions by varying the molar ratio of lower acyl radicals to hydroxyl radicals in the reaction mixture 75 from about 1/1 to about 10/1. Similarly, mixed glycerol esters containing two higher acyl radicals and one lower acyl radical can be prepared in proportionately high amounts within Group 3 compositions by varying the 80 molar ratio of lower acyl radicals to hydroxyl radicals in the reaction mixture from about 1/1 to about 10/1.

The relative amount of higher acylated triglyceride, such as a fat or an oil, is an 85 additional variable in the present process, this variable largely determining the proportion of the above described four reaction product Groups in the reaction mixture after the present reaction. The relative 90 amount of higher acylated triglyceride in the reaction mixture can be expressed as the molar ratio of higher acyl radical to the sum of the lower acyl and hydroxyl radicals

(e.g. $\frac{\text{acetyl} + \text{hydroxyl}}{\text{stearyl}}$ ratio). Although a 95

wide range of such ratios can be employed to prepare Group 2 and Group 3 compositions, ratios ranging from about 1/10 to 100 10/1 are more generally employed in the reaction mixture. When the process is employed to prepare maximum amounts of Group 2 compositions, ratios ranging from about 1/10 to about 1/1 are preferably 105 employed. To prepare proportionately high amounts of Group 3 compositions, ratios of about 1/3 to about 10/1 are preferably employed.

Varying yields of Group 2 and Group 3 110 compositions can be obtained by varying the relative amount of higher acylated triglyceride in the reaction mixture as described above. However, complete conversion of the reactants to the desired reaction product 115 Group is approached by re-cycling the distillates and distillation residues not comprising the Group being separated. As the high temperature basic transesterification catalyst is not substantially destroyed or inactivated during the reaction or by the successive distillations, additional amounts of catalyst need not be added to the system. Thus, a continuous type of reaction is facilitated as there is not a build-up of inactivated catalyst materials in the system. 125

The present invention provides a new and improved cyclic process which is eminently suited for the preparation of the mixed glycerol ester compositions of commerce, 130

typical of such compositions being the aforementioned "acetylated monoglycerides". The present process can be readily utilised to prepare and separate specific "tailor-made" compositions from the diversity of reaction products resulting from the reaction of the components in the herein described reaction mixtures.

Further, the present cyclic process can be effected without objectionable decomposition of the reactants to produce products substantially free of objectionable discoloration. Likewise, the products of the present invention are substantially free of catalyst materials, these catalyst materials often times occurring as undesirable impurities in related products prepared in accordance with other processes.

WHAT WE CLAIM IS:—

1. An improvement in or modification of the method claimed in Claim 1 of British Patent No. 745,566 comprising reacting together a triglyceride containing higher acyl radicals having at least eight carbon atoms and a hydroxyl radical-containing reactant which is either a mixture of glycerine with a triglyceride containing lower acyl radicals having from two to six carbon atoms or a glycerol partial ester composition comprising glycerine and a mixture of lower acylated glycerine the lower acyl radicals having from two to six carbon atoms, said reaction being effected in the presence of a basic transesterification catalyst, subjecting the resulting reaction mixture to a first vacuum distillation effective to separate therefrom a first distillate containing the remaining portions of said hydroxyl radical-containing reactant, subjecting the residue from first distillation to thin film vacuum distillation effective to separate therefrom a second distillate containing a substantial amount of a mixed glycerol ester having at least one of said higher acyl radicals and at least one of said lower acyl radicals, combining the residue from said second distillation with the first distillate and with make-up material comprising additional amounts of said triglyceride containing higher acyl radicals and said hydroxyl radical-containing reactant, and repeating said sequential steps.
2. A process as claimed in Claim 1 in which the first distillation is effected by thin film vacuum distillation.
3. A process as claimed in either of Claims 1 or 2 in which the triglyceride containing lower acyl radicals is triacetin.
4. A process as claimed in either of Claims 1 or 2 in which the glycerol partial ester composition containing lower acyl radicals is an acetylated glycerol partial ester composition.
5. A process as claimed in either of Claims 1 or 2 in which the triglyceride containing lower acyl radicals is tributyrin.
6. A process as claimed in either of Claims 1 or 2 in which the glycerol partial ester composition containing lower acyl radicals is a butyrate glycerol partial ester composition.
7. A process as claimed in any one of the preceding claims in which the reaction is carried out at a temperature at least 180°C.
8. A process as claimed in Claim 7 in which the reaction is carried out at a temperature in the range 230°C. to 260°C.
9. A process as claimed in any one of the preceding claims in which the basic transesterification catalyst is a bivalent alkaline earth hydroxide catalyst.
10. A process as claimed in any one of the preceding claims in which the triglyceride having higher acyl radicals is lard or hydrogenated lard.
11. A process as claimed in any one of Claims 1 to 10 in which the first distillate contains only the remaining portions of said hydroxyl radical-containing reactant and the mixed glycerol ester of the second distillate contains only one of said higher acyl radicals.
12. A process as claimed in Claim 11 in which the residue from the second distillation is distilled to give a distillate containing a mixed glycerol ester having two of said higher acyl radicals.
13. A process as claimed in any one of Claims 1 to 10 in which the first distillate contains in addition to said hydroxyl radical-containing reactant, a mixed glycerol ester containing only one of said higher acyl radicals and the second distillate contains a mixed glycerol ester containing two of said higher acyl radicals.
14. A process as claimed in any of Claims 1 to 10 in which the first distillate contains only the remaining portions of said hydroxyl radical-containing reactant and the second distillate contains glycerol esters having one and two of said higher acyl radicals.
15. A process as claimed in any one of the preceding claims in which the molar ratio of the higher acyl radicals to the sum of the lower acyl radicals and hydroxyl radicals in the reaction mixture ranges from 1/10 to 10/1 and the molar ratio of the lower acyl radicals to the hydroxyl radicals in the reaction mixture ranges from 1/10 to 120/1.
16. A process as claimed in Claim 15 in which the molar ratio of the higher acyl radicals to the sum of lower acyl radicals and hydroxyl radicals in the reaction mixture ranges from 1/10 to 1/1, the molar ratio of lower acyl radicals to hydroxyl radicals in the reaction mixture ranging from 1/5 to 5/1.
17. A process as claimed in any one of

the preceding claims in which the reaction mixture is continuously withdrawn from a reaction zone, the withdrawn reaction mixture is continuously subjected to said first distillation, said first distillate is continuously re-cycled into the reaction zone, the second distillation residue is continuously re-cycled into said reaction zone and additional amounts of said make-up material are continuously introduced into said reaction zone.

18. A process as claimed in Claim 17 in

which the make-up materials and the second distillate comprise substantially equal amounts of materials and have substantially equal proportions of higher acyl radicals, lower acyl radicals and hydroxyl radicals.

19. A process for preparing mixed glycerol ester compositions as particularly described hereinbefore.

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